

Doping evolution of the superconducting gap structure in heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$: heat transport study

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We performed systematic thermal conductivity measurements on heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals with $0.747 \leq x \leq 0.974$. At $x = 0.747$, the κ_0/T is negligible, indicating nodeless superconducting gap. A small residual linear term κ_0/T ($\approx 0.035 \text{ mW/K}^2 \text{ cm}$) appears at $x = 0.826$, and it increases slowly up to $x = 0.974$, followed by a drastic increase of more than 20 times to the pure KFe_2As_2 ($x = 1.0$). This doping dependence of κ_0/T clearly shows that the nodal gap appears near $x = 0.8$, likely associated with the change of Fermi surface topology. The small values of κ_0/T from $x = 0.826$ to 0.974 are consistent with the “ γ ”-shaped nodal s -wave gap recently revealed by angle-resolved photoemission spectroscopy experiments at $x = 0.9$. Furthermore, the drastic increase of κ_0/T from $x = 0.974$ to 1.0 is inconsistent with a symmetry-imposed d -wave gap in KFe_2As_2 , and the possible nodal gap structure in KFe_2As_2 is discussed.

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To understand the pairing mechanism of electrons in superconductors, it is instructive to study the symmetry and structure of their superconducting gap. Due to the multiple Fermi surfaces (FSs), the situation in iron-based high-temperature superconductors is very complicated [1]. While many of them have nodeless superconducting gaps, clear evidences for nodal gap were found in some iron-based superconductors, such as KFe_2As_2 [2–5], LaFePO [6, 7], LiFeP [8], $\text{BaFe}_2(\text{As}_{1-x}\text{P}_x)_2$ [9–11], and $\text{Ba}(\text{Fe}_{1-x}\text{Ru}_x)_2\text{As}_2$ [12]. Clarifying whether the nodes are symmetry-imposed (like d -wave in cuprate superconductors) or just accidental is crucial for fully understanding the pairing mechanism in iron-based superconductors.

Among these nodal superconductors, one particular interesting case is KFe_2As_2 [2–5, 13, 14]. Unlike the optimally doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ which has both electron and hole FSs [15], only hole FSs (Γ -centered pockets and off- M -centered lobes) were found in the extremely hole-doped KFe_2As_2 [16]. Earlier thermal conductivity and penetration depth measurements unambiguously showed that KFe_2As_2 has nodal superconducting gap [2, 3]. Later, more detailed thermal conductivity study provided evidences for a d -wave gap [4]. The recent observation of sudden reversal in the pressure dependence of T_c was also interpreted as evidence for d -wave superconducting state in KFe_2As_2 at ambient pressure [13]. However, the laser angle-resolved photoemission spectroscopy (ARPES) experiments conducted at 2 K directly revealed the gap structure on the Γ -centered hole FSs: a nodeless gap on the inner FS, an unconventional gap with “octet-line nodes” on the middle FS, and an almost-zero gap on the outer FS, which showed that KFe_2As_2 is a nodal s -wave superconductor [5].

To investigate the doping evolution of gap structure

in heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ may shed light on this enigma. Recently, laser ARPES measurements on $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0.93, 0.88$, and 0.76) revealed systematic change of gap structure on the Γ -centered hole FSs upon Ba doping into KFe_2As_2 [17]. While the inner FS remains nodeless, the nodes gradually disappear on the middle FS upon Ba doping, and eight nodes clearly appear on the outer FS for all three dopings [17]. However, another ARPES group measured $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ with $x = 0.7$ and 0.9 [18, 19], and they did not find any nodes in all three Γ -centered hole FSs. While the gap in the M -centered electron pocket is nodeless for $x = 0.7$, a “ γ ”-shaped nodal gap was detected at the tip of the four off- M -centered small hole lobes for $x = 0.9$ [18, 19]. Therefore, there are two important issues of the superconducting gap in heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. One is at which doping level the superconducting gap changes from nodeless to nodal, and the other is what is the exact nodal gap structure in the heavily hole-doped regime. More experiments are highly desired to clarify these two related issues, which will also help to resolve the KFe_2As_2 enigma.

In this Letter, we present a systematic heat transport study of heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals with $0.747 \leq x \leq 0.974$. According to the doping dependence of the residual linear term κ_0/T , the nodeless to nodal gap structure change happens near $x = 0.8$, likely coinciding with the Lifshitz transition (change of the FS topology). The small values of κ_0/T from $x = 0.826$ to 0.974 are consistent with the peculiar “ γ ”-shaped nodal s -wave gap structure observed in Ref. [19]. A more than 20 times increase of κ_0/T from $x = 0.974$ to $x = 1$ is inconsistent with a symmetry-imposed d -wave gap in KFe_2As_2 . The large value of κ_0/T in KFe_2As_2 may be mainly caused by the drastic decrease of the slope

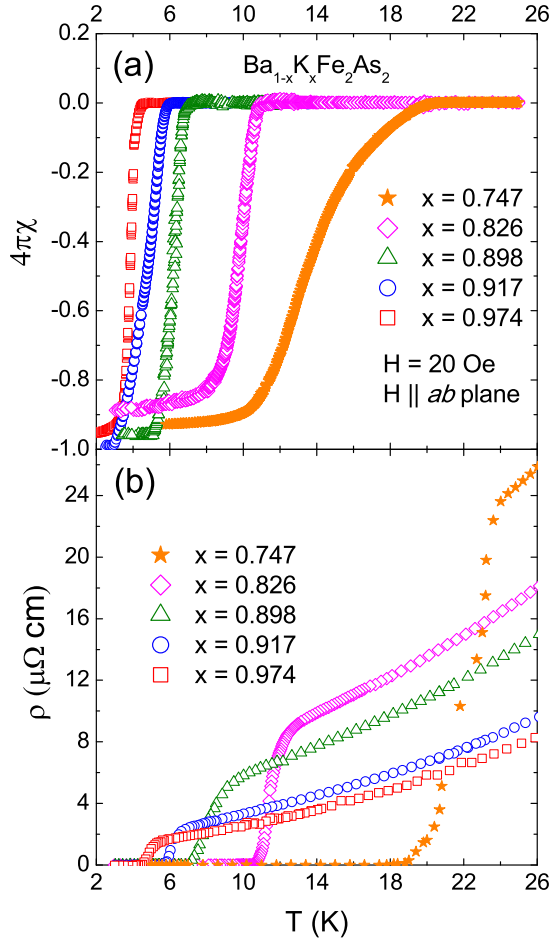


FIG. 1. (Color online) (a) The dc magnetic susceptibility of heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals with $x = 0.747, 0.826, 0.898, 0.917$, and 0.974 . (b) The low-temperature resistivity of these $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals. For each sample, the transition temperature T_c defined by $\rho = 0$ agrees well with the onset of the diamagnetic transition in (a).

of the gap at the node, i.e., changing from “ γ ”-shaped nodal gap to some kind of “ \vee ”-shaped.

Single crystals of heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ were grown by the self-flux method [20]. The compositions were determined by wavelength-dispersive spectroscopy (WDS), utilizing an electron probe micro-analyzer (Shimadzu EPMA-1720). The dc magnetic susceptibility was measured at $H = 20$ Oe, with zero-field cooling, using a SQUID (MPMS, Quantum Design). The samples were cleaved and cut into rectangular shape with large ab plane. Contacts were made directly on the sample surfaces with silver paint, which were used for both resistivity and thermal conductivity measurements. All samples were exposed in air less than 3 hours to avoid degradation. The contacts are metallic with typical resistance 30 mΩ at 2 K. In-plane thermal conductivity was measured in a dilution refrigerator, using a standard four-

TABLE I. The T_c , residual resistivity ρ_0 , residual resistivity ratio RRR, residual linear term κ_0/T , the fitting parameter α , and the normalized κ_0/T of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals with $x = 0.747, 0.826, 0.898, 0.917$, and 0.974 . The values of clean KFe_2As_2 single crystal are also listed [4].

x	T_c	ρ_0	RRR	κ_0/T	α	$\frac{\kappa_0/T}{\kappa_{N0}/T}$
	(K)	($\mu\Omega$ cm)		(mW/K ² cm)		
0.747	18.7	17.9	25	0	2.05	0%
0.826	10.8	6.15	57	0.035	3.34	0.88%
0.898	7.16	2.83	105	0.054	3.09	0.62%
0.917	5.66	1.38	176	0.106	3.15	0.60%
0.974	4.55	0.76	300	0.152	3.76	0.48%
1.0	3.80	0.21	1108	3.60	3	3.1%

wire steady-state method with *in situ* calibrated RuO_2 chip thermometers. Magnetic fields were applied along the c axis and perpendicular to the heat current. To ensure a homogeneous field distribution in the sample, all fields were applied at temperature above T_c .

Figure 1(a) shows the dc magnetic susceptibility of heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals with $x = 0.747, 0.826, 0.898, 0.917$, and 0.974 . The low-temperature resistivity of these $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals are plotted in Fig. 1(b). For each sample, the transition temperature T_c defined by $\rho = 0$ agrees well with the onset of the diamagnetic transition in Fig. 1(a). Table I lists their T_c , residual resistivity ρ_0 , and residual resistivity ratio RRR. The values of clean KFe_2As_2 single crystal are also listed [4].

Figure 2(a) presents the low-temperature thermal conductivity of the five heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ in zero field. To obtain the residual linear term κ_0/T , the curves are fitted to $\kappa/T = \kappa_0/T + bT^{\alpha-1}$ below 0.25 K [21, 22]. For $x = 0.747$, the fitting gives $\kappa_0/T = -5 \pm 9 \mu\text{W K}^{-2} \text{ cm}^{-1}$. Comparing with our experimental error bar $5 \mu\text{W K}^{-2} \text{ cm}^{-1}$, this value is negligible and we take it as zero. For $0.826 \leq x \leq 0.974$, the fittings gave finite but quite small κ_0/T , which are listed in Table I together with that of clean KFe_2As_2 sample [4]. The second term $bT^{\alpha-1}$ is normally contributed by phonons, and the typical value of α lies between 2 and 3 [21, 22]. However, as listed in Table I, the α values of $0.826 \leq x \leq 0.974$ samples are abnormally higher than 3, which will be discussed later.

In Fig. 2(b), we plot the doping dependence of T_c and κ_0/T for heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. While the T_c shows a smooth doping dependence, the doping evolution of κ_0/T is rather drastic [23]. The negligible κ_0/T at $x = 0.747$ suggests that it is still fully gapped, as the case of $x = 0.7$ [18]. A finite κ_0/T appears at $x = 0.826$, and increases slowly and monotonically up to $x = 0.974$. For a superconductor, the finite κ_0/T in zero field usually comes from the nodal quasiparticles [25]. Therefore,

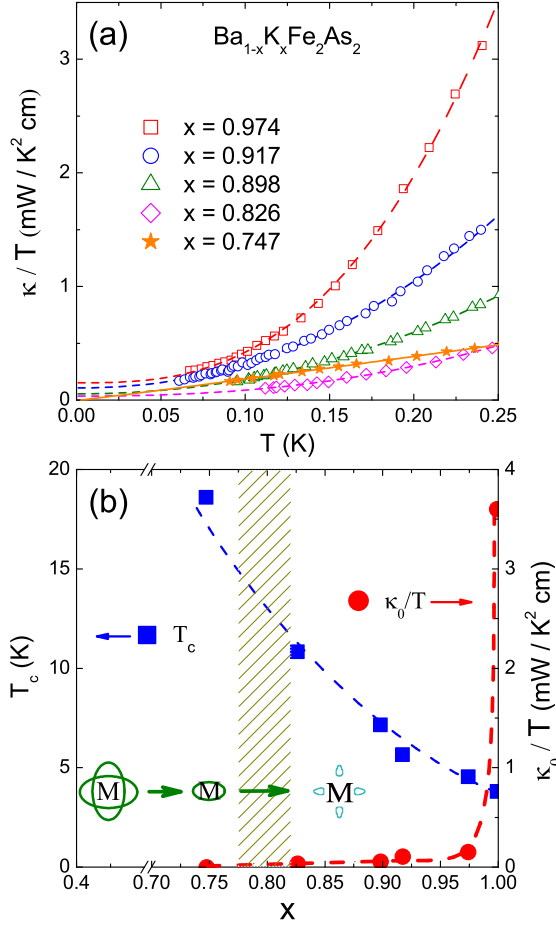


FIG. 2. (Color online) (a) Low-temperature in-plane thermal conductivity of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals in zero field. The dashed lines are fitting curves according to $\kappa/T = \kappa_0/T + bT^{\alpha-1}$. (b) Doping dependence of T_c and κ_0/T . The data of clean KFe_2As_2 single crystal are included [4]. The dashed lines are guide to the eye. The Lifshitz transition is roughly located inside the shadow area [19].

all these four samples have nodal superconducting gap. From $x = 0.974$ to $x = 1$, a more than 20 times increase of κ_0/T is observed. Below we discuss this systematic doping evolution of κ_0/T in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$.

First, this doping evolution of κ_0/T clarifies that the superconducting gap changes from nodeless to nodal between $x = 0.747$ and 0.826 . Previously, ARPES measurements show that there is a Lifshitz transition between $x = 0.7$ and 0.9 [18, 19]. The M -centered small electron pockets at $x = 0.7$ transforms into four off- M -centered hole lobes at $x = 0.9$ [18, 19]. While the superconducting gaps in all FSs of $x = 0.7$ sample are nodeless [18], there is a “ γ ”-shaped vertical line node on each tip of the off- M -centered hole lobes for $x = 0.9$ sample [19]. Therefore, our thermal conductivity result is consistent with these ARPES experiments, and further narrows down the doping range to $0.747 \leq x \leq 0.826$, where the superconducting gap changes from nodeless to nodal. This change is

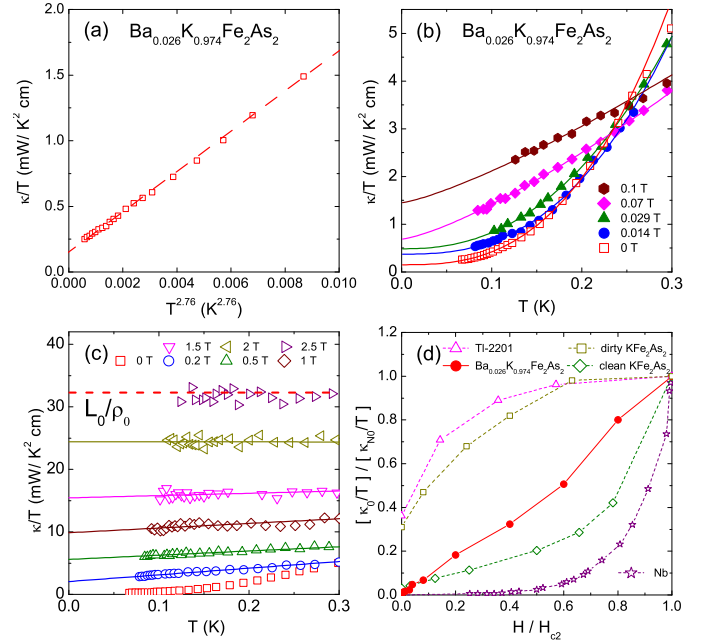


FIG. 3. (Color online) (a) Low-temperature in-plane thermal conductivity of $\text{Ba}_{0.026}\text{K}_{0.974}\text{Fe}_2\text{As}_2$ single crystal in zero field, plotted as κ/T vs $T^{2.76}$. (b) and (c) κ/T vs T for $\text{Ba}_{0.026}\text{K}_{0.974}\text{Fe}_2\text{As}_2$ single crystal in magnetic fields applied along the c axis. The solid lines are fits of the data to $\kappa/T = a + bT^{\alpha-1}$. For $H \geq 0.2$ T, the curves are roughly linear, and α is fixed to 2. The dashed line is the normal-state Wiedemann-Franz law expectation L_0/ρ_0 , with L_0 the Lorenz number $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ and $\rho_0 = 0.76 \text{ } \mu\Omega \text{ cm}$. (d) Normalized residual linear term κ_0/T of $\text{Ba}_{0.026}\text{K}_{0.974}\text{Fe}_2\text{As}_2$ as a function of H/H_{c2} . For comparison, similar data are shown for the clean s -wave superconductor Nb [28], the archetypal d -wave cuprate superconductor Tl-2201 [29], the dirty and clean KFe_2As_2 [2, 4].

very likely correlated to the Lifshitz transition [18, 19], as illustrated in Fig. 2(b).

Second, we note that κ_0/T is very small in the doping range of $0.826 \leq x \leq 0.974$ [23]. These values are only 0.48% to 0.88% of their normal-state Wiedemann-Franz law expectations L_0/ρ_0 , with $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. Theoretically, for a quasi-2D nodal superconductor, κ_0/T can be estimated from [26, 27]

$$\frac{\kappa_0}{T} = \frac{\pi^2 k_B^2}{3} N_F v_F^2 \frac{a \hbar}{2 \mu \Delta_0}, \quad (1)$$

in which N_F and v_F are the density of states in the normal state and the Fermi velocity, respectively. The parameter a depends on the gap symmetry, Δ_0 represents the maximum amplitude of the gap, and μ is the slope of the gap at the node [26, 27]. According to this formula, the small values of κ_0/T for $0.826 \leq x \leq 0.974$ may be explained by the special nodal s -wave gap structure observed in $\text{Ba}_{0.1}\text{K}_{0.9}\text{Fe}_2\text{As}_2$ by ARPES [19]. Since all of the Γ -centered hole FSs have nodeless gaps for $x = 0.9$ [19], there is no contribution to κ_0/T from these FSs.

Nodes are only located at the tips of the off- M -centered ε FS lobes [19]. The angular distribution of the superconducting gap manifests a special “ γ ” shape near the node, as seen in Fig. 4(c) of Ref. [19]. Comparing with the usual “ \vee ” shape near a d -wave gap node or the node observed in Ref. [17], the “ γ ” shape has a very large slope μ near the node, which may result in the very small κ_0/T in the doping range of $0.826 \leq x \leq 0.974$.

Furthermore, the special “ γ ”-shaped nodal s -wave gap structure may also explain the abnormally high fitting parameter α of the bT^α term in this doping range. Usually, the bT^α term is contributed by phonons, and α is between 2 and 3 [21, 22]. However, the α values of $0.826 \leq x \leq 0.974$ samples are higher than 3. More interestingly, this α is very sensitive to magnetic field. As seen in Fig. 3(b), a very small field of $H = 0.1$ T has suppressed α from 3.76 to 2.27 for $x = 0.974$ sample. The high sensitivity of α to field suggests its electronic origin. In fact, for nodal superconductors, the T dependence of thermodynamic quantities at low temperature depends on how the gap increases with the distance from the nodal point [30]. For clean d -wave superconductors, an electronic T^3 term of thermal conductivity was theoretically predicted [26], and indeed observed in ultraclean $\text{YBa}_2\text{Cu}_3\text{O}_7$ single crystal [31]. This electronic T^3 term was rapidly suppressed by magnetic field [31]. In this context, the “ γ ”-shaped nodal gap may result in an α value higher than 3, which needs to be theoretically verified. In Fig. 3(d), we plot the normalized κ_0/T of $\text{Ba}_{0.026}\text{K}_{0.974}\text{Fe}_2\text{As}_2$ as a function of H/H_{c2} , obtained from Figs. 3(b) and 3(c). The curve lies between the dirty and clean KFe_2As_2 , and is similar to those of RbFe_2As_2 and CsFe_2As_2 single crystals [32, 33]. For complex nodal s -wave gap structure of a multiband superconductor, with both nodal and nodeless gaps of different magnitudes, it is hard to get a theoretical curve of $\kappa_0(H)/T$.

Third, κ_0/T increases more than 20 times from $x = 0.974$ to $x = 1$. This is hard to be simply explained by the decrease of impurity scattering, since ρ_0 decreases rather smoothly, only about 3 times from $x = 0.974$ to $x = 1$. Since the Fermi surface topology does not change from $x = 0.9$ to $x = 1$ [16, 19], the superconducting pairing symmetry presumably remains unchanged at this doping regime. If this is the case, the drastic increase of κ_0/T from $x = 0.974$ to $x = 1$ is against the d -wave pairing symmetry proposed in Ref. [4], since it is inconsistent with the universal heat conduction of a d -wave gap. In fact, according to Eq. (1), Δ_0 is proportional to T_c , and N_F and v_F only change slightly in heavily hole-doped regime [34, 35]. The drastic increase of κ_0/T must result from a drastic decrease of μ . Therefore, while the decrease of impurity scattering may play some role, the drastic increase of κ_0/T may be caused by the change of nodal gap from “ γ ”-shaped to some kind of “ \vee ”-shaped. In this scenario, the Γ -centered hole pockets remain nodeless in KFe_2As_2 , which is in line with the gap structure of

$x = 0.9$ sample in Ref. [19] and different from the “octet-line nodes” of $x = 1$ sample in Ref. [5]. To finally resolve this issue, more low-temperature ARPES measurements on high-quality KFe_2As_2 single crystals, other than Ref. [5], are needed.

In summary, we have measured the thermal conductivity of heavily hole-doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals with $x \geq 0.747$, and got a monotonic but drastic doping dependence of κ_0/T . The absence of κ_0/T at $x = 0.747$ and the appearance of a very small κ_0/T (≈ 0.035 mW K $^{-2}$ cm $^{-1}$) at $x = 0.826$ indicates that the crossover from nodeless to nodal superconducting state occurs at $x \sim 0.8$, correlated to the Lifshitz transition. The very small κ_0/T and abnormally large α of the $x = 0.826$, 0.898, 0.917 and 0.974 samples are consistent with the special “ γ ”-shaped nodal s -wave gap structure observed in $\text{Ba}_{0.1}\text{K}_{0.9}\text{Fe}_2\text{As}_2$ [19]. The more than 20 times jump of κ_0/T from $x = 0.974$ to $x = 1.0$ may be mainly caused by the change of nodal gap from “ γ ”-shaped to some kind of “ \vee ”-shaped on the off- M -centered hole lobes.

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measured down to ~ 250 mK [24]. Their results are very different from ours. They observed non-monotonic doping dependance of κ_0/T , and the κ_0/T of their $x = 0.93$ and 0.88 samples ($T_c = 7.3$ and 11 K) are much larger than those of our samples with similar T_c .

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